

# Titan

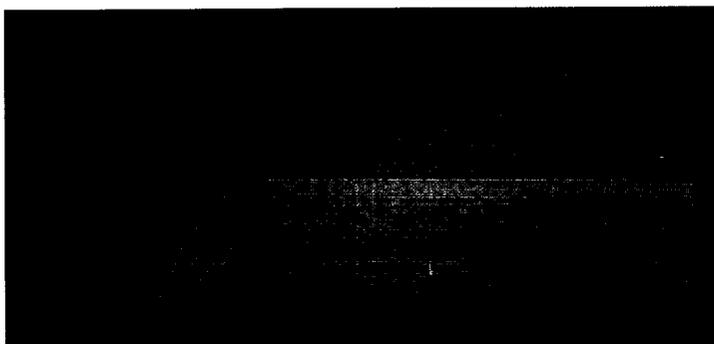
N 93 - 18553

T. Owen, D. Gautier, F. Raulin,  
and T. Scattergood

**T**itan is Saturn's largest satellite, with a diameter greater than that of Mercury and an atmosphere denser than Earth's. This atmosphere began as an assemblage of gases produced by the outgassing of the materials that accreted to form the satellite. Chemical reactions during the accretion process and over the subsequent eons produced the gases that we find today. In fact, the process is far from over: Titan offers us an enormous natural laboratory in which a variety of experiments in chemical evolution are taking place today.

We are, therefore, confronted with a kind of paradox. Here is a solid body, large enough to retain an atmosphere and small enough to allow hydrogen to escape, leading us to expect to find the same oxidizing conditions we encounter on the inner planets. Yet, unlike the atmospheres of those familiar bodies, Titan's atmosphere is highly reducing, consisting primarily of nitrogen, with methane the next most abundant reactive constituent.

ORIGINAL PAGE  
COLOR PHOTOGRAPH



The surface pressure is 1.5 bars and the surface temperature is close to 94 K. It is this low temperature that explains the paradox, since under these conditions water is totally frozen out so there is no readily available source of oxygen to change the character of the atmospheric chemistry. Even though methane is continually being dissociated and the resulting hydrogen escapes from Titan's exosphere, the reducing state of the atmosphere is maintained.

Nevertheless some CO and CO<sub>2</sub> are present, in addition to a large number of hydrocarbons, nitriles, and complex polymers that form a ubiquitous smog in Titan's lower stratosphere. Methane should condense to form hazes of crystals in the upper troposphere, while ethane clouds may exist at lower altitudes. Indeed, it is possible that sufficient ethane has been produced to form lakes, seas, or even a global ocean on the satellite's surface.

The chemistry that produces these various compounds has not yet been elucidated in detail. Is the CO primordial, or is it produced by reactions with infalling ice? What is the relative significance of magnetospheric electrons, galactic cosmic rays, and solar ultraviolet light in driving the chemical reactions? What level of chemical complexity has been achieved? For

example, are there polymers of HCN? Is adenine being produced? What relationship does this chemistry have to the various pathways postulated for prebiotic chemistry on the primitive Earth?

In this chapter, we shall review the current status of the analysis of Voyager and ground-based observations of Titan and the interpretation of these data in terms of laboratory experiments and theoretical models. We will conclude with a description of a proposed mission to advance our knowledge and some considerations of the significance of Titan from a planetary system perspective.

## Observations of the Atmosphere

Our knowledge of the structure and the composition of the atmosphere of Titan comes primarily from observations made by Voyager 1 in November 1980. The spacecraft passed Titan at a distance of 4000 km from its surface, making a wide variety of measurements with all of the instruments it carried.

Figure 7-1 gives a summary of the main physical characteristics of the satellite. The voyager radio occultation experiment achieved the first



Table 7-1: Characteristics of Titan

Surface radius	2575 km
Mass	0.022 Earth mass
Surface gravity	135 cm s <sup>-2</sup> (0.14 Earth gravity)
Mean density	1.881 g cm <sup>-3</sup> (0.34 Earth density)
Distance from Saturn	1.226 × 10 <sup>6</sup> km = 20 R <sub>S</sub>
Orbit period around Saturn	15.95 day
Orbit period around Sun	29.46 years
Obliquity	26°.7 (assumed equal to Saturn's)
Temperature	
Surface	94 K
Tropopause (42 km)	71.4 K
At 200 km altitude	~170 K (at the equator)
Surface pressure	1496 mbar

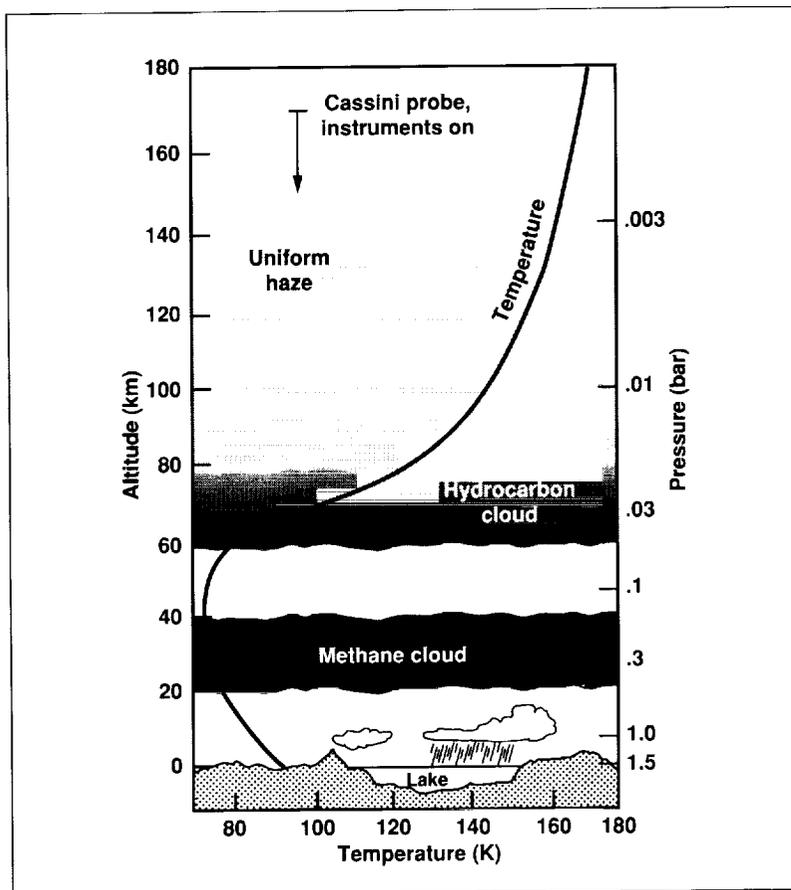


Figure 7-1. The temperature structure of the Titan atmosphere from early Voyager results. This approximate thermal profile has just been updated (see text); the landscape is drawn to demonstrate some of the possibilities that our present ignorance permits.

measurement of the radius of the solid surface of Titan which is hidden from view by layers of smog in the atmosphere. The optical limb of Titan, as defined by the smog, is at an altitude of 200 km, but layers of aerosols have been detected up to 500 km. The radio occultation experiment, combined with results from the Voyager infrared and ultraviolet spectrometers,

indicates that the main atmospheric component is molecular nitrogen. These data also provide a description of the vertical thermal structure of the atmosphere at Titan's equator. A recent reanalysis of the radio occultation data indicates that the surface temperature of

Titan could be between 92.5 and 101 K, the tropopause temperature between 71.4 and 74.5 K, and the stratospheric temperature between 164 and 172 K around the 160 km altitude level. The temperature profile above the 200 km altitude level is not known but is probably isothermal or weakly increasing with altitude at least up to 300 km (fig. 7-1).

A major part of the uncertainty identified in the reanalysis originates from lack of a precise value for the atmospheric mean molecular weight. As much as 20% of the atmosphere might consist of non-radiogenic argon, a mixture of isotopes with atomic masses 36 and 38. Argon is expected to be present for cosmogonical reasons, as we shall see below. Unfortunately, this gas is very difficult to detect directly from a remote vantage point. The only indication of its existence at present is a possible contribution to the mean molecular weight of the atmosphere. The present uncertainty in this quantity precludes any firm conclusions (see table 7-2).

Table 7-2: Stratospheric Composition of Titan

Gas	Mole fraction	Comments
Major components		
Nitrogen (N <sub>2</sub> )	0.757–0.99	
Argon (Ar)	0–0.21	Inferred indirectly
Methane (CH <sub>4</sub> )	0.005–0.034	May condense in the troposphere (0.002–0.21 at the surface)
Hydrogen (H <sub>2</sub> )	0.002–0.006	
Hydrocarbons		
Ethane (C <sub>2</sub> H <sub>6</sub> )	1 × 10 <sup>-5</sup>	At the equator
Acetylene (C <sub>2</sub> H <sub>2</sub> )	1.8 × 10 <sup>-6</sup>	At the equator
Propane (C <sub>3</sub> H <sub>8</sub> )	7.0 × 10 <sup>-7</sup>	At the equator
Ethylene (C <sub>2</sub> H <sub>4</sub> )	5.0 × 10 <sup>-9</sup>	At the equator
Diacetylene (C <sub>4</sub> H <sub>2</sub> )	10 <sup>-8</sup> –10 <sup>-7</sup>	At the north pole
	1.4 × 10 <sup>-9</sup>	At the equator
Nitriles		
Hydrogen cyanide (HCN)	1.4 × 10 <sup>-7</sup>	At the equator
Cyanoacetylene (HC <sub>3</sub> N)	10 <sup>-8</sup> –10 <sup>-7</sup>	At the north pole
Cyanogen (C <sub>2</sub> N <sub>2</sub> )	10 <sup>-8</sup> –10 <sup>-7</sup>	At the north pole
Oxygen compounds		
Carbon dioxide (CO <sub>2</sub> )	1.1 × 10 <sup>-8</sup> 3.3 × 10 <sup>-9</sup>	Assuming a constant mixing ratio At 108 km altitude level, assuming a distribution parallel to the one of Samuelson et al. (1983)
Carbon monoxide (CO)	6 × 10 <sup>-5</sup> <4 × 10 <sup>-6</sup>	In the troposphere In the stratosphere

Methane is clearly present in the stratosphere as indicated by its features in the infrared spectrum. In fact, this gas was detected spectroscopically in the troposphere 45 years ago with the 2.1-m reflector of the McDonald Observatory. The CH<sub>4</sub> stratospheric molar abundance is between 0.5 and 3.4%. Near-infrared ground-based measurements unfortunately do not provide accurate estimates of the CH<sub>4</sub> abundance in the tropo-

sphere. It is generally considered, although not on a firm basis, that the CH<sub>4</sub> abundance at the surface is around 5-10%. Since CH<sub>4</sub> may condense at the tropopause, its tropospheric mixing ratio cannot be deduced from the stratospheric value, except if the latter is less than the tropopause saturation value. The lower limit in the troposphere is then 0.5%. If argon is included in maximal proportions, the upper limit of

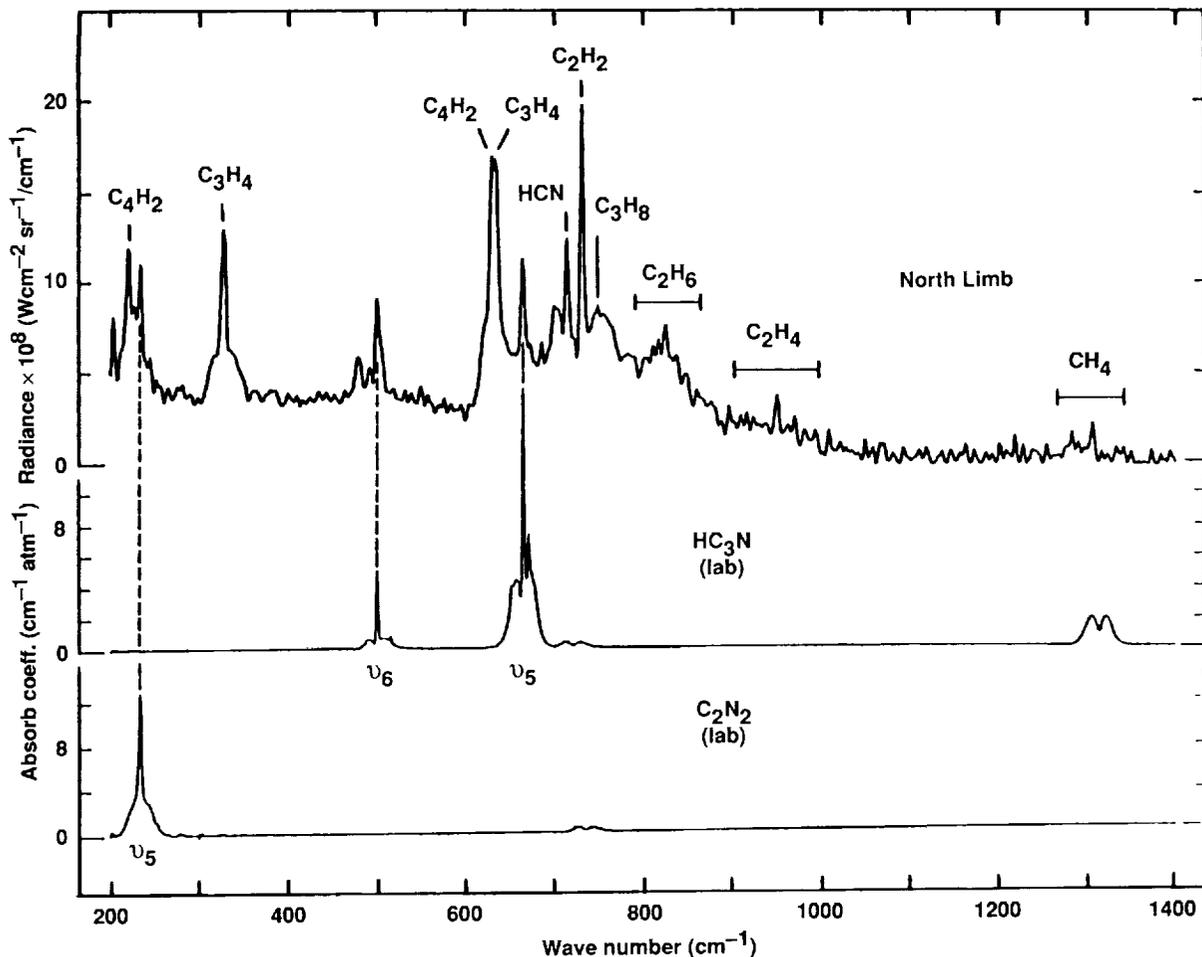
the CH<sub>4</sub> molar abundance at the surface may be as high as 21%; if argon is absent, the maximum value is reduced to 11.7%. The stability of the atmosphere requires unsaturated relative humidities in the lower atmosphere; CH<sub>4</sub> clouds are expected somewhere between the ground and the tropopause level.

The infrared spectra recorded by the Voyager IRIS (Infrared Imaging Spectrometer) experiment have also revealed the presence of hydrocarbons and nitriles in the stratosphere of Titan (fig. 7-2 and table 7-2). These species are formed from the dissociation of  $\text{CH}_4$  and  $\text{N}_2$ .

The stratospheric abundances of  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_2$ , and  $\text{HCN}$  at the equator have recently been revised taking advantage of new improvements to the determinations of the equatorial thermal profile and of more precise laboratory measurements of band intensities and other spectroscopic parameters. Most of the planetary emission in the

observed bands originates from about the 108 km altitude level, except for the  $\nu_5$  band of  $\text{C}_2\text{H}_2$  which is formed at an altitude around 130 km. (Note that all stratospheric minor components, except  $\text{CO}$ , condense below 50 to 70 km altitude levels.) The abundances observed at these levels are systematically

Figure 7-2. A section of Titan's infrared spectrum as recorded by the Voyager IRIS instrument.



higher than predicted by detailed photochemical models except for  $C_2H_4$  and  $CO_2$  for which the agreement is satisfactory. This does not necessarily imply that present photochemical models must be revised, however. In the procedure used in these models to calculate the mixing ratios of various stratospheric species above the saturation level, the magnitude of the eddy diffusion coefficients in the lower thermosphere and in the lower stratosphere play a key role. A readjustment of these coefficients may permit the predictions from the models to be reconciled with the observations.

More constraints come from near horizontal viewing observations made by Voyager 1 at the north pole of the satellite. Spectra were recorded at various altitudes, allowing the retrieval of vertical distributions of stratospheric absorbers. Vertical distributions of  $C_2H_2$ ,  $C_2H_6$ ,  $C_3H_4$ ,  $C_4H_2$ , HCN, and  $HC_3N$  have thus been obtained. All species exhibit mixing ratios increasing with height, at least up to the 300-400 km altitude level, except  $C_2H_6$  for which the concentration holds fairly constant above the saturation level. Some distributions have shapes, but not amplitudes, compatible with photochemical models. That is the case

for  $C_2H_6$ ,  $C_4H_2$ ,  $HC_3N$ , and  $C_3H_4$ , but not for  $C_2H_2$  and HCN. It must be noted that the models refer to the whole disk of Titan while the north pole photochemistry may be peculiar because of the geometrical configuration in this region. That this peculiarity is not caused primarily by seasonal effects may be seen by a more detailed examination of the spatial distribution of stratospheric constituents.

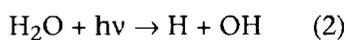
No longitudinal variation in temperature or abundances was detected at the equator. On the other hand, HCN,  $HC_3N$ ,  $C_2N_2$ ,  $C_4H_2$ , and  $C_3H_4$  appear to be strongly enhanced at the north pole compared to the equator. Moreover, comparison of IRIS spectra at the north and south poles suggests that abundances of nitriles are similar in the two regions, at least on the night side. That confirms the special nature of the photochemistry at the poles, but rules out explanations based on seasonal effects.

The case of CO is especially intriguing. It is unusual to find an oxygen-containing compound in this reducing environment, and the vertical distribution of CO in Titan's atmosphere is itself something of a puzzle. CO was discovered in the near infrared by ground-based observations. A  $CO/N_2$  mixing ratio of about  $6 \times 10^{-5}$  was derived. The observed lines are believed to be formed mainly in the troposphere of the satellite. Since CO does not condense at Titan's temperatures, its mixing ratio is expected to be constant with height up to very high atmospheric levels. However, recent millimeter heterodyne observations lead to the conclusion that the stratospheric mixing ratio cannot exceed  $4 \times 10^{-6}$ . The only way to reconcile the near-infrared and microwave observations is the possibility that CO is severely depleted in the stratosphere compared to its abundance in the troposphere. Such behavior is in conflict with presently available models of Titan that consider CO to be uniformly mixed throughout the whole atmosphere. The main difficulty is how to maintain a vertical gradient in the presence of even a minimal vertical mixing, considering the stability of the CO molecule.

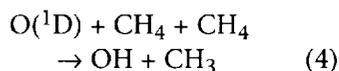
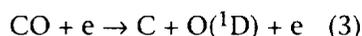
The CO that we find on Titan today may either be original or formed by reactions with H<sub>2</sub>O that enters the atmosphere from the outside in the form of ice crystals or meteoritic dust. A similar ambiguity exists for the production of CO<sub>2</sub>. This molecule is produced from CO and OH, mainly through the reaction



Once again the oxygen (in the form of OH) can either come from ice:



or it could be contributed from the (primordial) CO:



where O(<sup>1</sup>D) is the excited state of atomic oxygen.

Another perspective on these possibilities is furnished by the evidence for an enhanced value of D/H in Titan's atmosphere. The abundance ratio CH<sub>3</sub>D/CH<sub>4</sub> on Titan seems to require the preservation of an interstellar value

of D/H in the volatiles incorporated in the satellite, because processes acting since the formation of Titan will not produce the observed enrichment. If this is indeed true, then one might expect some residue of the interstellar dominance of CO over CH<sub>4</sub> to remain in the gases produced during the accretion of Titan. In fact, the methane we find on Titan today may not be interstellar methane at all, but rather the result of the accretional heating (during Titan's formation) of organic compounds trapped in interstellar grains. Whether or not the CH<sub>4</sub> is original, the high D/H suggests the CO may well be, in which case one would expect an amount roughly equivalent to the N<sub>2</sub> abundance we find today in the atmosphere. Reactions 1-4 will cause the irreversible conversion of CO to CO<sub>2</sub> which we should find deposited on the surface today.

## Laboratory Simulations and Theoretical Models of Titan's Atmosphere

**W**hat we know about the composition of Titan's atmosphere is certainly incomplete.

In the absence of detailed, *in situ* measurements of the actual constituents and energy source, investigators have turned to laboratory experiments and computational models that simulate the physics and chemistry that are believed to be taking place. Each of these approaches has its limitations but both can be used separately, or preferably, in concert to make predictions about the processes responsible for the observed atmospheric species (table 7-2) and about species not yet observed, but which should be looked for by future probes sent to Titan (table 7-3).

Table 7-3: Upper Limits on Abundance of Nitriles Expected to be Present in Titan's Atmosphere

Nitriles	Mole fraction
Acetonitrile (CH <sub>3</sub> -CN)	<2.5 × 10 <sup>-7</sup>
Propionitrile (C <sub>2</sub> H <sub>5</sub> -CN)	<5.0 × 10 <sup>-7</sup>
Acrylonitrile (CH <sub>2</sub> =CH-CN)	<2.0 × 10 <sup>-7</sup>
Crotononitrile (CH <sub>3</sub> -CH=CH-CN)	<4.0 × 10 <sup>-8</sup>
Allylcyanide (CH <sub>2</sub> =CH-CH <sub>2</sub> -CN)	<4.0 × 10 <sup>-8</sup>
Methacrylonitrile (CH <sub>2</sub> =C(CH <sub>3</sub> )-CN)	<7.5 × 10 <sup>-8</sup>
Cyanopropyne (CH <sub>3</sub> -C≡C-CN)	<2.5 × 10 <sup>-7</sup>

An important example of the deductions that have been made indirectly (which will require confirmation) is the possibility of an ethane ocean. Such an ocean is postulated to cover much, if not most, of Titan's surface and to contain compounds formed in the atmosphere. The existence of this ocean is based upon both theoretical modeling and laboratory studies of the photochemistry of methane, the most abundant hydrocarbon in Titan's atmosphere. Such studies suggest that ethane will be the predominant product of methane photochemistry and will condense at the low temperature prevailing over Titan's surface. More details about this putative ocean will be given below.

Most of the laboratory studies that have been done thus far to examine the chemistry and physics of Titan's atmosphere can be divided into two broad classes. The first class consists of experiments that are carried out to provide specific data needed to interpret spectroscopic and optical observations of Titan or for inclusion in theoretical models of atmospheric physics and chemistry. Examples would be laboratory spectra of gases to identify features in Titan's spectrum and the determination of rate constants for specific chemical reactions.

The second class of laboratory experiments is more general in scope. These are attempts to simulate various types of chemical processes expected to occur in different regions of Titan's atmosphere. Most of these experiments have been done for the purpose of developing reasonable scenarios for explaining the compounds that have already been detected on Titan. In these studies, mixtures of CH<sub>4</sub>, N<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub> which represent models of Titan's atmosphere are subjected to various sources of energy, including ultraviolet light, electric discharges (simulating lightning and plasmas associated with meteor infall), and energetic electrons or protons representing those trapped in radiation belts around Saturn. After exposure of the gas mixtures to the appropriate energy source, the products are separated from the initial reactants and their chemical identities and yields are determined. These yields can then be compared to the amounts of the various species found on Titan in order to assess the roles that different chemical processes play in the chemistry of the atmosphere.

For example, when mixtures of  $N_2$  and  $CH_4$ , in proportions similar to those found on Titan (table 7-2), were subjected to bombardment by energetic electrons (simulating processes in the upper atmosphere) or to electric discharges (hypothesized to occur in the troposphere), all of the nitriles and hydrocarbons detected on Titan were formed. Oxygen compounds and argon have not yet been included in these experiments. In addition, many other compounds including  $C_3$ ,  $C_4$ , and  $C_5$  hydrocarbons and nitriles were made. Certain of these compounds, for example acetonitrile ( $CH_3CN$ ) and allene ( $CH_2CCH_2$ ), were produced in amounts relative to  $HCN$  and  $C_2H_2$ , respectively, that are similar to those of some of the species already observed in Titan's atmosphere. Most of the nitriles exhibit far-infrared absorption bands so that it is possible to estimate the upper limits of their abundances from Voyager IRIS spectra as shown in table 7-3. These upper limits, compared with abundances of detected nitriles ( $HCN$ ,  $HC_3N$ , and  $C_2N_2$ ) are compatible with values expected from laboratory simulations. A number of complex organic heteropolymers could also be present.

On the other hand, the very idea has been challenged that magnetospheric electrons are responsible for the breaking of the  $N_2$  bond (required to initiate formation of nitriles). The penetration depth of such electrons might be so small that they can only be involved in chemical processes occurring at high altitudes where organic molecules are not protected enough against photodissociation. Instead, galactic cosmic rays (GCR) could play a crucial role in these syntheses. Modeling studies suggest that the absorption of high energy GCR in the 0.1-50 mbar region of the atmosphere can generate energetic electrons that are able to induce several reactions driving the photochemistry. By coupling of the nitrogen and hydrocarbon chemistry, these processes can lead to the formation of  $HCN$  and other N-organics. Presumably reactions involving  $CO$  would also be initiated, although these have not yet been studied. This possibility is especially attractive in view of the mysterious deficiency of  $CO$  in the stratosphere (see above).

Finally, almost all of the experiments discussed above included the formation of solid/liquid products, often called tholins. These materials are generally reddish-brown to reddish-orange and may represent some of the substances that constitute the hazes and clouds that exist on Titan. Analyses of these materials show them to consist of a very complex mixture of hydrocarbons, nitriles, and other compounds but a definitive confirmation of the composition of any laboratory tholins has yet to be achieved.

In addition to laboratory simulations, modeling of the physics and chemistry of planetary atmospheres can be accomplished by the use of theoretical computations. Mathematical expressions representing the detailed steps in a chemical scheme are combined to "simulate" the process under study. Examples of this approach applicable to Titan include numerous models of the photochemistry of the atmosphere (discussed below), models of the effects of high-energy particles on the chemistry of the upper atmosphere, models of the scattering of light by aerosols (helpful in understanding the nature of the light that is reflected back to us from the satellite), and models

describing the ways in which energy is transmitted and radiated by the atmosphere. Only the first two types of models will be discussed here as these explicitly involve the chemistry that can explain the species observed on Titan and those that may be present but not yet found.

Theoretical studies on the photochemistry of  $C_1$  and  $C_2$  hydrocarbons were first done in the mid-1970s. A model was developed several years later for the photochemical conversion of  $NH_3$  (which may have been the initial form of nitrogen on Titan) into the  $N_2$  found today. We have already referred to the very comprehensive and detailed model that includes all of the important features of previous work developed in the mid-1980s. This model includes the photochemistry of all of the hydrocarbons, nitriles, and oxygen compounds listed in table 7-2, plus the chemistry initiated by the influx of energetic

particles from the magnetosphere, but not the effects of GCR. Some 150 elementary reactions are included, yielding a model with both advantages and disadvantages over the simpler models. The inclusion of such a large number of reactions reduces the chances of inadvertently leaving out important reactions, but the uncertainties in the results may be considerably increased owing to the need for rate constants for all of the reactions. Many of these reaction constants are only poorly known or are not known at all and must be estimated. This becomes especially critical when the particular reaction that controls the overall rate of the chain is either overlooked or poorly estimated. Even with these limitations, the photochemical models are quite useful in understanding the chemistry of Titan's atmosphere, in predicting compounds to search for, and in establishing the locations in the atmosphere in which to carry out such searches.

Summarizing the results of this model, all of the presently detected species in Titan's atmosphere can reasonably be accounted for by photochemical and energetic-particle driven reactions.

However, the authors recognized that many of the reactions are only poorly understood and some uncertainties exist about certain details of the results. For example, a model suggests that large amounts of allene should be formed but none has been detected thus far. Also, as we pointed out above, this model in its original form does not give close agreement with the most recent evaluation of atmospheric abundances and distributions of other known species. Finally, except for the polyacetylenes, no compounds with more than three carbon atoms are included in the model, thus little can be said about the formation and nature of the known aerosols.

Photochemical models do indicate that large amounts of ethane (and some other organic compounds) should have been produced over Titan's history, thus leading to the idea that the satellite's surface may be covered by a global ethane ocean. The properties and ramifications of such an ocean will be discussed in the following section.

# Endpoints of Atmospheric Chemistry: Aerosols and Oceans

As mentioned above, most of the compounds present in the gas phase must condense in the lower stratosphere because of the cold temperature. In this region, and around the tropopause, the concentration of condensable trace constituents in the gas phase must be very low. For example, all the nitriles, including HCN, have mole fractions smaller than  $10^{-15}$  at altitudes ranging from 60 km down to 10 km.

The condensation of the low molecular weight organics would be induced by the submicrometer particles formed in the higher regions of the atmosphere through photopolymerization of  $C_2H_2$ ,  $C_2H_4$ , and HCN. (The latter may actually polymerize on aerosol surfaces, rather than in the gas phase; a point that needs additional clarification.) These particles, of mean radius around 0.01 to 0.1 micrometers, would be responsible for the haze layers observed in the 200-400 km region. After precipitation down to the lower atmospheric layers, they would act as nucleation centers, allowing the conden-

sation of lower molecular mass compounds. The resulting aerosol clouds would consist of particles covered by an external layer of more volatile organics and having a mean radius increasing with decreasing altitude.

The physical modeling of the processes that control the formation and vertical distribution of aerosols in Titan's atmosphere, as performed before the Voyager Mission, did not use the right atmospheric conditions. A new model has recently been developed which is based on a microphysical approach and uses an up-to-date atmospheric profile. It considers coagulation, condensation, diffusion, and precipitation processes, starting from a submicrometer particle in the high stratosphere. It includes the eventual vaporization of a part of the aerosol in the lower troposphere. Preliminary results obtained from this model indicate that there may be a permanent rainfall down to the surface of aerosol droplets with average diameters up to a few hundred micrometers. This is in agreement with the results of a recent multiple scattering radiative transfer model. Near the surface of Titan, a typical

aerosol particle would consist of a core of several tens of micrometers which is mainly composed of nitriles and covered by an envelope consisting of  $C_1$  to  $C_3$  hydrocarbons. In these droplets, most of the organics would be highly enriched relative to the atmosphere. For instance, the concentration of  $C_2$  and  $C_3$  hydrocarbons would be three orders of magnitude higher in the aerosol close to the surface than those in the atmosphere.

Very close to the surface, most of the methane in the aerosol would be vaporized, feeding the lower troposphere with this compound. The resulting near-surface increase of the atmospheric methane mole fraction should lead to the condensation of this compound on Titan's surface, in order to maintain a quasi-thermodynamical equilibrium between surface and atmosphere.

Atmospheric methane is rapidly photolyzed, either directly in the mesosphere or catalytically through acetylene photolysis in the stratosphere. Given the first discovery in 1944 of CH<sub>4</sub> in Titan's atmosphere and repeated detection since, it seems very unlikely that we have been observing a very peculiar phase of Titan's history, where methane would have suddenly been abundant in the atmosphere. On the contrary, it can be assumed that methane must have been present in the current large amount in Titan's atmosphere during most of the history of this planetary body. This requires the existence of a CH<sub>4</sub> reservoir on Titan's surface.

The presence of a pure CH<sub>4</sub> ocean could play this role. However, previous analyses of data from the Voyager radio occultation experiment seem to indicate the absence of such an ocean, at least of a global ocean. But this does not rule out the presence of a methane-ethane ocean. In fact, this hypothesis appears to be the best model of Titan's surface at the present time.

Effectively, the major net product of methane photolysis is ethane. Because of the low atmospheric temperatures, ethane, like most other organics, condenses near the tropopause. It remains in a condensed phase down to low altitudes where it should be a

liquid. Consequently, Titan's surface could be covered by an ocean of liquid ethane which could contain enough methane to act as the sought-for reservoir. The presence of methane in liquid ethane markedly decreases the atmospheric methane abundance and provides atmospheric conditions which are consistent with the observational data.

If we assume that the ethane flux downward to the surface has been roughly constant for the past 4.5 billion years and equal to the present photolytical rate of ethane production ( $5.8 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ ), then the minimum depth of the resulting ocean would be about 700 m. This ocean would be composed primarily of residual methane plus the ethane produced photochemically. It could be a global ocean, with this average depth, or it could be broken up into isolated lakes, depending on the topography. This latter scenario is consistent with recent radar measurements of Titan which show variations in "brightness" with rotation of the satellite. However, some have argued that Titan must either have a global ocean or no ocean at all, i.e., no large discrete bodies of liquid on its surface, to avoid changes in its orbit from tidal dissipation. We shall speak of this possible accumulation of liquid on Titan's surface as an

ocean, for simplicity. This ocean should contain a noticeable fraction of dissolved gases (mainly nitrogen and, if present in the atmosphere, argon). It should also include additional solutes, in particular, organics coming from the atmosphere, either in the liquid or solid phases.

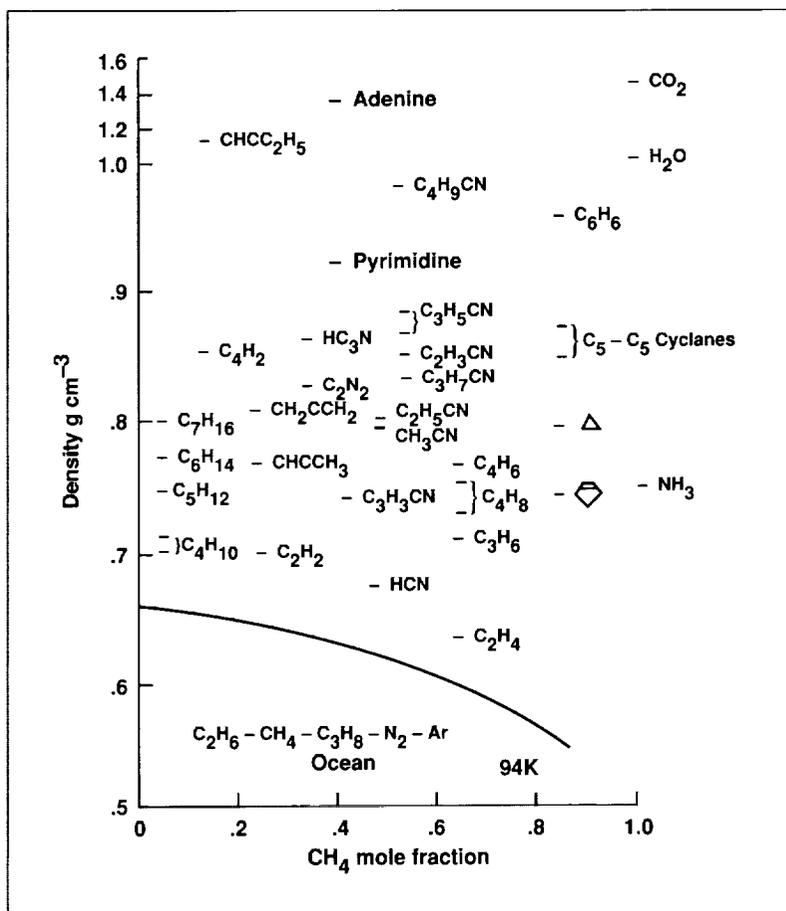
If one assumes that the ocean is in thermodynamic equilibrium with the adjacent atmosphere, knowing the surface temperature and the near-surface atmospheric composition, it is possible to calculate the bulk composition of the ocean. Using this approach, it is estimated that methane atmospheric mole fractions of 0.016 and 0.03 should correspond to methane mole fractions in the ocean of 0.13 and 0.25, respectively. In the latter case the mole fraction of dissolved nitrogen is about 0.05. Calculations on phase equilibria in the N<sub>2</sub>-CH<sub>4</sub>-C<sub>2</sub>H<sub>6</sub> system under Titan conditions indicate that equilibrium between such a ternary liquid system and Titan's atmosphere at 94 K implies an atmospheric CH<sub>4</sub> mole fraction ranging from 0.095 to 0.2. In this case, the ocean composition varies from CH<sub>4</sub> (0.86) to N<sub>2</sub> (0.03), respectively. These calculations do not take into account the possible presence of argon. In addition they also ignore the likely presence of other solutes in the ocean.

Now the aerosols will continuously and irreversibly feed the lower troposphere, and finally the ocean, with ethane, but also with other organics. Few of these are in the liquid state at the temperature of the surface. But propane ( $C_3H_8$ ) will be a liquid and is miscible in very large proportions in the methane-ethane ocean. If we assume that the flux of propane, like that of ethane, has been roughly constant during all of Titan's history and is equal to  $1.4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ , then the mole fraction of propane in the ocean,  $f(C_3H_8)$ , is proportional to that of ethane. Thus, the main composition of the ocean should be  $CH_4-C_2H_6-C_3H_8-N_2-CO-(Ar)$ , with  $f(C_3H_8) = 0.024 \times f(C_2H_6)$ . Most of the other compounds transferred to the ocean by means of the aerosols should be solid at the temperature of the surface. Depending on their density relative to the ocean they will either sink or float. In addition, depending on their solubility and their atmospheric flux to the surface, they must dissolve partly or totally. Thermodynamic modeling of these processes has recently been carried out, first by considering the case of a few of the low molecular weight organics and a  $C_2H_6-CH_4$  solvent, neglecting the presence of dissolved  $N_2$  and other gases, then by considering a  $C_2H_6-CH_4-N_2$  solvent

and a larger variety of solutes. The results suggest that all the non-dissolved solutes should be denser than the ocean even if its main constituents include argon and propane with high mole fractions (fig. 7-3). Thus the surface of Titan's ocean should be free of any organic icebergs.

The ocean would be very rich in organic solutes, with concentrations in the range 1 to  $10^{-6} \text{ mole l}^{-1}$ , depending on their chemical nature. With the exception of alkanes and cyclanes, which are very soluble in such a solvent, most of the other solutes, taking into account their plausible atmospheric

Figure 7-3. a) The curved line gives the density of the ocean as a function of its methane mole fraction (atmospheric argon mixing ratio = 0.17; oceanic propane mole fraction relative to ethane = 0.024). b) The labeled dashes show the densities of various possible solutes at the same temperature (94 K).



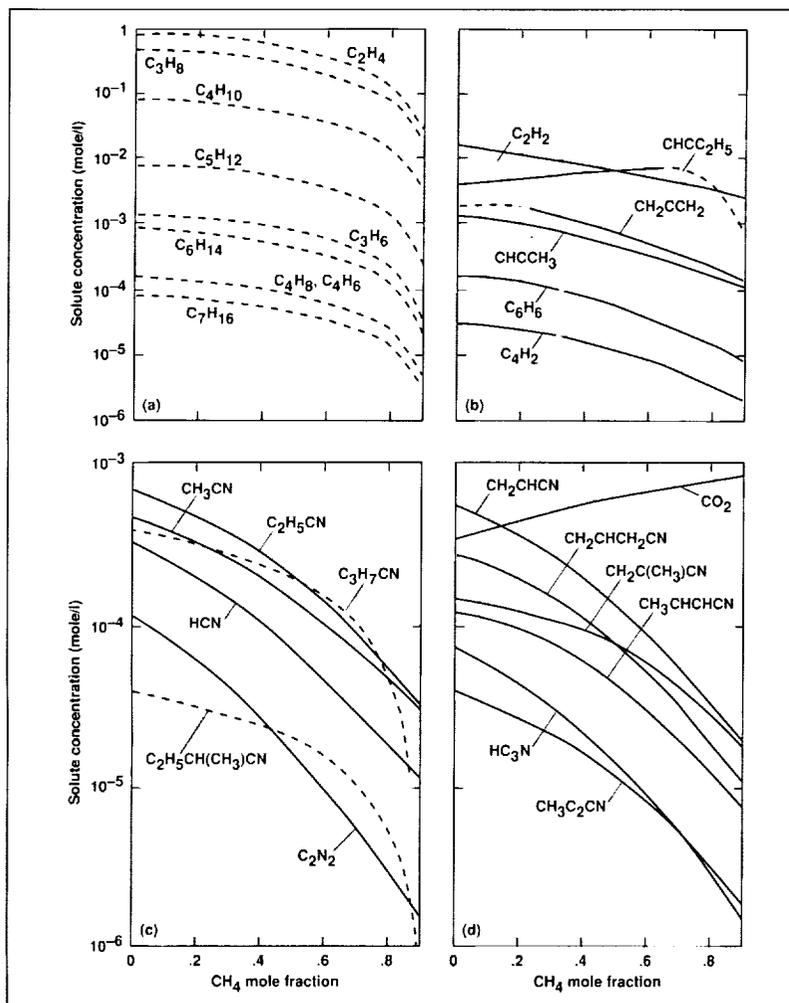


Figure 7-4. Estimated concentration of selected solutes as a function of methane mole fraction in the ocean (94K, argon free). a & b: hydrocarbons; c: alkylnitriles; d: other nitriles and carbon dioxide. (Dashed line indicates that saturation is not reached).

flux, will reach saturation. This is the case, in particular, of acetylene, the solubility of which ranges between about  $10^{-2}$  mole  $l^{-1}$ , corresponding to a mole fraction of about  $4 \times 10^{-4}$  (for an ethane-rich ocean), and  $3 \times 10^{-3}$  mole  $l^{-1}$ , corresponding to a mole fraction of about  $10^{-4}$  (for

a methane-rich ocean). For the nitriles, which are more polar than the alkynes and consequently less soluble in this apolar solvent, the solubilities are smaller. They range between  $10^{-3}$  and  $10^{-6}$  mole  $l^{-1}$ . For instance, the saturation concentration of HCN would be about

$3 \times 10^{-4}$  mole  $l^{-1}$  in an ethane-rich ocean, and  $10^{-5}$  mole  $l^{-1}$  in a methane-rich ocean (fig. 7-4). The solubilities should be also very temperature dependent.

For the high molecular weight compounds the solubility must be very low, especially if the ocean is ethane rich. The only polymer slightly soluble in such a solvent seems to be polyethylene, and only in a methane-rich ocean. Thus a deep layer of organic compounds, mainly acetylene, HCN, and their oligomers or hetero-oligomers, should be present at the bottom of Titan's ocean. Such a reservoir of organics should buffer the oceanic concentration of these compounds.

But this milieu is not static. It should be a dynamic organic chemical environment. Its surface is continuously bombarded by galactic cosmic rays of very high energy (higher than a few 10 GeV) not absorbed by the atmosphere. Such particles could induce new reactions in this exotic ocean by processes analogous to those recently studied in the case of Triton. From this stage chemical evolution on Titan must follow a path very different from the terrestrial one: a chemical evolution in which liquid water is replaced by a cryogenic apolar solvent.

# Titan and Exobiology

Despite this important difference from Earth, Titan remains an extremely interesting solar system object for exobiological studies. The interest obviously arises from the opportunity this satellite provides for the study of on-going organic synthesis under totally natural conditions over an immense span of time. The absence of liquid water also removes a readily available source of the oxygen that is required for many fundamental biochemical compounds, as we discussed above. Nevertheless the presence of CO, possibly as a primordial abundant gas, leaves open the possibility of more prevalent syntheses involving oxygen compounds in the past. Here the low temperature and reducing conditions are an advantage; unless there really is a global ocean, ancient materials should be well-preserved and readily accessible on Titan's surface.

Looking back over Titan's history, we note the possibility that ammonia was present during the early epochs and might even have been the precursor of the N<sub>2</sub> that we now find in the atmosphere. Hence, all of the simple molecules normally postulated as the necessary ingredients for prebiotic synthesis

(CH<sub>4</sub>, NH<sub>3</sub>, CO, N<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>) were probably available. There is even a possibility of more moderate temperatures (say 200 K) if sufficient ammonia were present to cause a large greenhouse effect. This would have been a short-lived condition since ammonia is so easily dissociated, but that process itself would have produced some interesting compounds as fragments combined with other radicals in the atmosphere and on the surface.

At the present time, however, we must confine ourselves primarily to reactions involving C, N, and H. Of particular interest here are syntheses starting with HCN and HC<sub>3</sub>N, both of which are known to be present on Titan. The question is whether or not the resulting polymers are of any interest to prebiotic chemistry. Adenine can be synthesized from hydrogen cyanide dissolved in ammonia. One can then ask whether this same synthesis can be achieved in the conditions existing in Titan's atmosphere or in the reservoirs of liquid hydrocarbons on the surface.

The time scale available becomes very important. The evolution of complex chemical systems over very long periods of time is difficult to model because of the uncertainties—no matter how small—about the exact reaction mechanisms and the rate constants. Thus the lakes or oceans on Titan may contain not only dissolved HCN but also some NH<sub>3</sub> formed from the irradiation of N<sub>2</sub> and H<sub>2</sub> by cosmic rays. With almost no time limitation, the formation of adenine and other purines on Titan cannot be excluded in spite of the low surface temperatures.

All of the purines and pyrimidines found in DNA and RNA have been identified in organic matter in meteorites, but how they were formed remains a mystery. The discovery of such compounds—or others of equal or greater complexity—on the surface of Titan would provide valuable insights into the nature of low-rate chemical and physical processes for the formation of organic compounds in a well-defined natural environment. These insights could then be used in conjunction with laboratory experiments to understand the prebiological chemistry on the primitive Earth. The changes in atmospheric composition on Titan over geologic time and the possibility that reaction products from ancient times are well-preserved on Titan's surface adds to the exobiological interest in future investigation of this giant satellite.

## The Next Steps

To make real progress from our present position we need answers to some fundamental questions that have been raised by the observations available to date. Is that hypothetical ocean really there? What is its composition, depth, and lateral extent? What landforms are present and to what extent are they coated with precipitated aerosols? What is the composition of these aerosols and how exactly are they produced?

This last question leads us directly into the problem of chemical evolution in the atmosphere. We are looking here for evidence of any preferred pathways from nitrogen, methane, and carbon monoxide to more complex substances. To define such pathways and to understand the atmospheric chemistry we also need to know what other trace constituents are present and what sources of energy are available at different altitudes and latitudes. What causes the evident differences between the chemistry occurring at the poles and near the equator? What is responsible for the hemispheric difference in the reflectivity of the aerosol layer? Is there additional chemical processing at the

surface driven by GCR or escaping internal heat? What can the noble gas abundances and their isotopic ratios tell us about the origin and evolution of Titan's atmosphere?

This list of questions can be extended for several pages, but the items already cited are sufficient to show the need for a new mission that returns to the Saturn system to make additional measurements. This mission should include a Saturn orbiter and a Titan probe. The orbiter would carry a radar mapper to define the satellite's surface topography and an array of infrared and microwave spectrometers to determine atmospheric composition and its variations with altitude and latitude. The probe would have a GCMS (Gas Chromatograph Mass Spectrometer) for studying gas composition connected to an aerosol pyrolyzer to analyze solid and/or liquid materials. A laser diode spectrometer could provide additional chemical analysis while defining the altitudes and scattering properties of clouds and hazes. A radar altimeter and a descent imager would furnish information on the nature of the surface during the probe's descent while, after landing, the GCMS could provide additional information on surface composition.

Both the probe and the orbiter would carry a variety of additional experiments as well, but the complement described above would already give us the basic information we seek. Just such a mission, called Cassini after the first director of the Paris Observatory who made many discoveries through his studies of the Saturn system, is currently planned as a joint enterprise between NASA and the European Space Agency. The Cassini Mission, with its Huygens probe into Titan's atmosphere, is scheduled for a late 1996 or early 1997 launch.

While we are awaiting the Cassini Mission there are still more observations that can be made from Earth. Among these, we point out the opportunity over the next decade for radar studies of Titan with the Arecibo and Goldstone antennas which should be able to determine whether or not a global ocean is present. There are also a number of additional infrared, submillimeter, and passive microwave observations that can be made as the sensitivity of detectors and the size of available telescopes increases during the next few years.

But there is simply no substitute for being there, so we look forward to the prospect of results from the Cassini Mission early in the next century.

## Conclusions

The importance of Titan goes far beyond the exobiological aspects we have emphasized here. This satellite may be viewed as a member of a class of icy-rocky objects that includes comet nuclei and the planetesimals that formed the cores of the giant planets as well as the icy satellites that surround them. Studying the volatiles on Titan, trying to understand their origin, and investigating the subsequent chemical reactions they undergo will provide insights into a variety of other solar system objects as well.

Nevertheless, Titan's significance for exobiology may be its most outstanding characteristic. The opportunity to investigate the results of contemporary chemical reactions in a reducing atmosphere under totally natural conditions is a little like the anthropologist's dream of studying a primitive tribe that has been kept completely out of contact with any advanced civilization. It is even difficult to know in advance exactly what we will learn, and that too is part of the attraction this shrouded world presents.

## Additional Reading

Hunten, D. M.; Tomasko, M. G.; Frasar, F. M.; Samuelson, A. F.; Strobel, D. F.; and Stevenson, D. J.: Titan. *In* Saturn, T. Gehrels and M. S. Matthews (eds.), Univ. of Arizona Press, Tucson, 1984, pp. 671-759.

Lunine, J. I.; Atreya, S. K.; and Pollack, J. B.: Present State and Chemical Evolution of the Atmospheres of Titan, Triton and Pluto. *In* Origin and Evolution of Planetary and Satellite Atmospheres, S. K. Atreya, J. B. Pollack, and M. S. Matthews (eds.), Univ. of Arizona Press, Tucson, 1989, pp. 605-665.

Owen, T.: The Composition and Origin of Titan's Atmosphere. *Planetary and Space Science*, vol. 30, 1982, pp. 833-838.



ORIGINAL PAGE  
COLOR PHOTOGRAPH

